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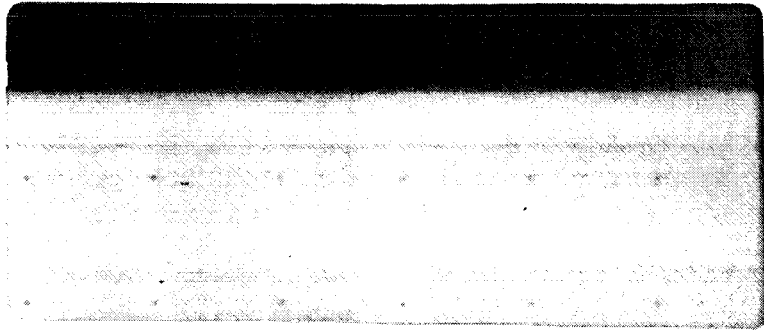
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*out*  
Research & Development Study  
of the Silver-Cadmium Couple for  
Space Application

Report No. 2

NASA

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Prepared by:

*Allen Charkey*  
Allen Charkey

*Allen Charkey 1963 27 p refs*

*G.A. Dalin*  
Dr. G.A. Dalin

Approved by:

*Frank Solomon*  
Frank Solomon, AVP

# TABLE OF CONTENTS

|                                    | <u>Page No.</u> |
|------------------------------------|-----------------|
| I. COVER                           |                 |
| II. TITLE PAGE                     |                 |
| III. TABLE OF CONTENTS.....        | 1               |
| IV. PURPOSE.....                   | 2               |
| V. ABSTRACT.....                   | 3               |
| VI. RESEARCH PROGRAM.....          | 4               |
| BODY OF REPORT.....                | 5               |
| 1. Phase 1.....                    | 5               |
| 2. Phase 2.....                    | 9               |
| 3. Phase 3.....                    | 12              |
| 4. Phase 4.....                    | 13              |
| VII. PROGRAM FOR NEXT QUARTER..... | 15              |

### P U R P O S E

The purpose of this program is to investigate the electrode reactions which take place in a sealed silver oxide-cadmium cell under satellite cycling regimes. The information will then be used in improving design and construction in a final 30-cell battery.

ABSTRACT

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The construction of most cells is complete. Some cells have begun a series of deep cycles to determine voltage and capacity characteristics at various temperatures. Special dummy cells have completed evaluation cycling; weights and surface areas of the test electrodes were measured. Results show considerable shedding at low electrolyte concentrations and large increases in surface area.

A test has been initiated to correlate separator attack by silver, with changes in composition of KOH electrolyte at 50°C.

Work on the mechanism of gas recombination has been started with study of the rate of O<sub>2</sub> diffusion through the electrolyte and through membranes, and, O<sub>2</sub> reduction at a mercury electrode. Sealed cells for a study of recombination under actual operating conditions have been constructed.

During this quarter a new type of positive electrode with a highly porous sintered matrix was developed, which shows promise for operation on the argentous level. Construction of cells with palladium and lead additives for single level cycling is also near completion.

The study of chemical reactions occurring at the AgO electrode during constant potential charging is under way.

Construction of automatic cycling equipment for evaluating cell performance under satellite conditions has been completed; most of this equipment is already in use.

As an accessory to the above, development of a device for automatically removing individual cells from a series changing circuit as they reach a specified voltage is under way. This is particularly necessary for the 100 minute orbit cycling.

AUTHOR

### THE RESEARCH PROGRAM

A description of the four phases into which the research program was divided was given in the first quarterly. For convenience, this is summarized below.

#### Phase 1

Study of the characteristics of the silver and cadmium plates of various constructions and composition. Effect of various separator materials on the AgO-Cd couple.

#### Phase 2

Investigation of rates of gas evolution and mechanism of recombination as a function of separator systems, and plate constructions. Effect of trickle charging with respect to pressure variations.

#### Phase 3

Study of physical and chemical changes occurring at the silver electrode during long constant potential charging.

#### Phase 4

Feasibility of operation of cells on the Ag<sub>2</sub>O plateau during long and short orbit cycling regimes.

## BODY OF THE REPORT

### Phase 1

#### 1.1 Dummy Test

As part of the study of the reactions occurring at the positive and negative electrodes, plates were given 10 deep cycles as "dummies". A variety of silver and cadmium plate constructions were investigated in this test. The purpose of the work in dummies was to separate the electrode reaction from extraneous factors such as the effect of separator, changes in electrolyte concentration during cycling, and the ratio of positive active material to negative. In each dummy cell, the test electrode occupied a central position between two bare counter-electrodes. In the case of silver the counter-electrodes were of silver, and for cadmium the counter-electrodes were fine nickel mesh. Prior to assembling of the dummies, each plate was weighed and its surface area was measured by determination of double layer capacitance. After cycling, the plates were reweighed and surface areas again were determined.

Thirty eight dummies, in 19 pairs, were constructed; odd numbered cells were cycled at current densities corresponding to the 24-hour orbit, and even numbered cell cycles corresponded to the 100-minute orbit.

With respect to the silver electrodes, it can be seen from Table I that the low density silver plates which were run on the long orbit regime shorted before the higher density materials. It should also be noted here that all the dummy cells run on the long orbit regime shorted by cycle 7. This is not surprising since the cycle frequency is low so that the time involved was relatively long. During this extended period the silver oxide in suspension and in solution oxidized the cell case walls forming conductive paths and eventually shorts. The KOH concentration did not appear to be a factor in the cycle life.

Turning now to the short orbit regime, cell 2 which was filled with 31% KOH maintained the best capacity throughout the temperature range tested. Also, no shorting was encountered on this more rapid regime.

So far as the cadmium electrodes are concerned only the pressed CdO and pasted CdO proved to be cohesive; the others disintegrated during the first charge. Even these, however, gave erratic results, probably because of the lack of pressure. Due to this lack, the cadmium formed into a bulky sponge which was quite uneven in thickness.

In view of the difficulties encountered, it was decided to suspend work on dummy cells and to pursue this phase of the study in regular cells only.

However, useful information was garnered in two important areas, namely, loss of positive active material (shedding) as a function of electrolyte concentration and plate density, and secondly change in surface area on the positive electrode with cycling.

Figure 1 shows the loss of active material on the positive electrodes after 10 cycles. It was found that the rate of shedding of silver is a function of electrolyte concentration; in addition, weight loss increases as the density of the plate decreases. The data indicate that maximum shedding occurs in the area of 31% KOH. This may be attributed to the fact that the solubility of  $\text{Ag}_2\text{O}$  is a maximum at a concentration between 28% - 33% KOH, ( $4.8-4.6 \times 10^{-4} \text{N}$ ).

Surface area measurements by double layer capacitance were made on the various types of silver electrodes before and after cycling; the results are presented in Table II. Also, in a separate experiment, the surface area of a silver plate was determined which had undergone 400 shallow cycles (equivalent to approximately 150 deep cycles) to find how prolonged cycling affects the surface area.

The calculated increases in area are so large as to call the method used into question. The curves obtained by imposing cathodic pulses on green silver plates show the conventional portions, so that calculation of the capacitance is straightforward. Moreover, the values are in reasonable agreement with that obtained by gas adsorption (BET). Consequently, the values for green plates would seem to be reliable.

However, at the end of the cathodic pulse for cycled plates, the voltage, in each case, decreased rapidly. This could be attributed to a reduction reaction. Cycled plates, which had been tested in a presumably discharged condition were, accordingly, broken open for examination. In some cases, black spots, taken to be argentous oxide, were found. The plates were heated to 300°C and held at that temperature for 2 hours. This treatment did not change the form of the transient.

Nevertheless, the drop in voltage following the pulse was assumed to be the result of a reduction. The initial slope of this section of the curve was taken as the measure of a pseudo-capacitance in parallel with the capacitance of the double layer. This pseudo-capacitance was subtracted from the measured total capacitance in calculating the area values shown in Table II.



It is not certain that this method of calculation is better than a first order approximation because the capacitances may not be additive linearly. To improve the DLC method reliability, plates will be subjected to cathode pulses to effect reduction, prior to the DLC measurement. Changes in calculated DLC and changes in the slope of the curve following the transient can then be correlated with the number and size of the cathode pulses. In addition, confirmation will be sought from other methods of measurement. BET will be run on the cycled plates. Also, we have made arrangements to attempt to compare cycled plates with green plates by electron diffraction.

It has been our experience that plates made from pasted cadmium oxide and pressed cadmium oxide show differences in performance. To find whether cadmium plates prepared from other materials might show advantages, plates were prepared from cadmium carbonate and from cadmium hydroxide, and included in the dummy and cell tests.

Unfortunately, the plates made from these materials would not accept charge (probably due to poor conductivity between the compound and the grid) either as individual plates or when fabricated into actual cells.

In an additional test a new type of cadmium electrode was prepared by electro-plating cadmium on a fine nickel grid from a  $\text{CdSO}_4/\text{H}_2\text{SO}_4$  plating bath. The electroplated negative was assembled in a test cell between two wrapped positives and discharged at a rate of  $400 \text{ ma/in}^2$  - see Figure 2. The results show an increase in capacity of about 15% over our standard pressed  $\text{CdO}$  plate. The big advantage of this type of plate stems from the fact that it showed no tendency to oxidize when taken out of the bath. For the first time, an easily prepared dry charged  $\text{AgO-Cd}$  cell thereby becomes possible.

The effect of conductive additives such as Shawinigan Black and graphite was also studied by means of the dummy negative plates made from pressed  $\text{CdO}$ . No increase in capacity was noted in single electrodes. These additives are also being studied in full cells.

## 1.2 Cell Tests

Plate constructions and electrolyte concentrations similar to those set up in dummies were also run in cells. Forty-six cells were constructed, each consisting of 3 positives and 4 negative electrodes; the design was such that the positive electrode limited the cell capacity. The cells, all of which were sealed and fitted with gauges and valves, are being put through a series of 10 evaluation cycles at three temperatures, i.e.,  $-15^{\circ}\text{C}$ , RT, and  $+50^{\circ}\text{C}$ . Regime cycling will follow. Four separator systems are being studied to determine effects on voltage characteristics, life performance and separator degradation. The four combinations are (starting from the positive plate) 2 nylon/6 Cl9, (Cl9 is a specially treated cellophane developed by Yardney Chemical Co.) 1 nylon/2 PVA/3 Cl9, 2 nylon/3 PVA, and 1 nylon/1 XPE (BAI material) 150/5-Cl9.

Capacity performance of the cells will be determined by subjecting the cells (grouped as 4 cell batteries) to cycling on 100 minute and 24 hour orbit regimes. Periodically the cells will be deep discharged and monitored by means of a multi-point recorder to determine changes in capacity. During charge (which will be constant current to 1.60 volts) the cells will be scanned by means of a motor driven selector switch. Each cell will be shut off individually when the pre-set voltage is reached, thus avoiding accidental, and uncontrolled overcharge more effectively than by conventional means. To date the cells have completed two formation cycles at room temperature; pertinent cycle data will be presented in the next quarterly report.

## 1.3 Investigation of Changes in Properties of Separator Materials

Data obtained from cells run at  $25^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  by Inland Testing Corp. under Air Force Contract #33(616)-7529-contractor Yardney Electric Corp. afford information concerning separator attack by electrolyte and oxidation by the silver electrode in sealed silver-cadmium cells.

Table III shows the cell electrolyte analyses after cycling; initially all cells were filled with 38% KOH. Table IV presents the layer by layer analysis of the silver content in the separator. The cells at  $25^{\circ}\text{C}$  completed about 1500 cycles at 50% depth of discharge, those at  $50^{\circ}\text{C}$  completed 90 cycles at 25% discharge depth before failure. It was found that at  $50^{\circ}\text{C}$  the PVA was so deteriorated that the exact area could not be measured. The figures in parenthesis in Table IV were obtained by dividing the actual amount of silver by the total area of one turn of separator. The real silver content in the PVA is higher than indicated as part of the PVA was lost by adherence to the adjacent layers. It can be seen that the electrolyte analyses of the four cells run at  $25^{\circ}\text{C}$  showed a relatively high concentration of free KOH; this is in sharp contrast to the cells cycled at  $50^{\circ}\text{C}$ . Note the high concentration of  $\text{K}_2\text{CO}_3$  found

in the second group of cells; this indicates a strong attack of the separator by electrolyte. Silver penetration and attack was severe at elevated temperatures; as was stated above, the PVA separator was almost completely degraded. It is concluded that time at high temperature rather than number of cycles is the important factor in capacity loss at high temperature. A second important factor is probably state of charge.

A test has been initiated to accumulate additional information concerning the reactions governing separator deterioration. In this experiment cells will be fabricated with various separator systems including G19, PVA, and irradiated grafted polyethylene films produced by Radiation Applications Inc; the cells will be filled with 31 and 42% KOH. The cells will stand in charged condition at 50°C until the free KOH concentration drops below 15%. Electrolyte will be sampled at regular intervals and titrated potentiometrically. It is hoped that the rate of separator attack can be correlated with the quantity of free KOH and the rate of formation of potassium salts (organic and inorganic) produced in the cells during stand.

#### Phase 2

A principal problem in the operation of sealed cells is the prevention of excessively high pressures during overcharge. Since in most cases the cells are positive-limiting, i.e. oxygen is produced at the end of charge, therefore, the major emphasis must be put on the reaction of cadmium with oxygen.

The reaction with oxygen goes through several stages. Part of the oxygen evolved at the surface of the silver goes into solution and the remainder goes into the head space above the electrolyte. Some of the oxygen may pass through the separators by diffusion and then continue to diffuse through the electrolyte in the negative compartment eventually reaching the negative electrode. Here again at least two reactions appear to be involved; in the first stage oxygen reacts with cadmium to form cadmium oxide, and in the second stage cadmium oxide reacts with cadmium and water to form cadmium hydroxide. For the oxygen in the head space to react, it must redissolve in the electrolyte in the negative compartment and then diffuse to the electrode. Finally, where part of the electrode is not completely coated with electrolyte as is the case in a starved cell, oxygen diffuses through the gas phase to make contact with the electrode at the meniscus between the electrolyte and the electrode. This is known to be the region of greatest reaction velocity. A still further mechanism is available as initially proposed by Baars and amplified by the researchers at Gulton, namely the mechanism which involves a reaction on the surface of the nickel which is normally present.

It was originally postulated that the reaction could take place completely on the surface of the nickel. The researchers at Gulton have taken the position that atomic hydrogen is present on the surface of the nickel and that this then reacts with the oxygen. Reduction of oxygen to peroxide as an intermediate is also generally accepted. Counting up the materials involved, it can be seen that, at the least, oxygen, hydrogen (atomic), hydrogen peroxide, potassium hydroxide, cadmium, cadmium oxide and cadmium hydroxide must be considered. As will be pointed out below adsorption of organic material on the surface of the cadmium is also a factor.

It thus becomes clear that the reaction mechanism from beginning to end is sufficiently complex so that a study based on the overall mechanism cannot be very meaningful by itself. We have therefore started a series of experiments designed to establish rates and mechanisms for individual steps in the overall process. In the first of these we have determined polarization curves for the reaction on the surface of the cadmium in the presence and in the absence of oxygen. In this experiment, gas was bubbled through a solution containing a sheet cadmium electrode, that is one that was not porous; currents, both anodic and cathodic were passed through the electrode, and the voltage vs.  $Hg/HgO$  reference electrode was measured by means of a luggin capillary. The right hand curve on Figure 3 shows the results obtained when oxygen was bubbled through the electrolyte. The potential at zero current corresponds reasonably closely to that of the reversible open circuit voltage.

The experiment was repeated, using nitrogen to sweep out all traces of oxygen from the system; the potential at zero current flow was about 150 millivolts more positive. This potential difference is due to the presence of impurities such as traces of metallic elements in the system. When the voltage was changed by passage of current in either direction, polarization also accounted for part of the potential difference. What is significant here is the fact that the presence of oxygen eliminates polarization regardless of the source so that in effect the electrode becomes much more reversible. This phenomenon might be due to the possible formation of cadmium hydroxide in the presence of oxygen whereas possibly only cadmium oxide is formed in its absence. Cadmium oxide is known to passivate the electrode, whereas cadmium hydroxide does not.

It is our intention to continue this phase of the work using potentiostatic methods and cyclic voltamperometry.

Although it has always seemed evident that the rate at which oxygen diffuses through the separators must be very small compared to the overall recombination rate, the actual rate has never been measured to our knowledge. To make measurements of this rate, a single layer of separator was clamped between 2 half-cells (physical half-cells, not electro-chemical half-cells).

In the left half was placed electrolyte, a green silver plate with a lead, a luggin capillary and a tube for introducing gas. In the right half cell was placed mercury to the depth of about one centimeter connected to a wire lead. The leads were connected to a source of potential. In the first experiments, PVA was used as the separator. The silver plate was made positive to the extent of 1.1 volts. At this potential practically no current flowed when nitrogen was passed through the solution to remove traces of oxygen. In a series of tests, oxygen was passed through the solution, and the current was measured. In the first experiments currents as high as 3 milliamps per square inch were generated, but in later experiments it was found that the actual current was much lower. It appears that the history of the separator may be involved. Particularly, it seems that where PVA was used, quantities of material had been extracted from the separator by the KOH and that this material could be adsorbed on the surface of the mercury.

Following up this idea one step further, a similar experiment was run without separator. In this arrangement, the mercury was present as a pool on the bottom of the cell. Voltage-current curves were then run on the polarograph. For contrast, the experiment was repeated with electrolyte which had been allowed to remain in contact with PVA. The results are shown on Figure 4. It is evident that the limiting current density is much greater for electrolyte which has not had any contact with PVA. It can only be concluded that material extracted from the PVA has been adsorbed on the surface of the mercury thus interfering with the reaction with oxygen.

It is planned to repeat this experiment with cadmium sheet to determine the effect of the adsorbed material on the rate of the reaction with cadmium. As part of this experiment, the electrolyte from a previously cycled cell will be studied with respect to its effect on the rate of the reaction of oxygen with cadmium.

The data which we have obtained thus far on the rate of diffusion of oxygen through the separator and on the rate of diffusion of oxygen through the electrolyte indicates that rates are so low that recombination of oxygen with cadmium in which either of these processes is involved will be negligible. Consequently, we propose to carry this work only far enough to determine the order of magnitude.

The next step should be to determine what is happening at the surface of the electrode. In this phase of the work we shall also investigate the effect of adsorbed materials on the electrode. The use of a rotating disc electrode consisting of pure cadmium sheet (non-porous) is being considered. This type of experiment can be used to separate the effect of diffusion from the rate of reaction at the surface. Pure electrolyte, and electrolyte containing reaction products from the separators will be studied. For the second stage of this work we shall then study the reaction of oxygen with cadmium in porous form. Special attention will be given to cadmium electrodes without nickel or other additives so that possible effects of hydrogen on the nickel will be eliminated.

To study such effects as positive plate density, negative plate density, additives to catalyze recombination, separator type, and concentration and quantity of electrolyte on gas recombination, 30 sealed cell units have been built. Formation cycles have been completed. Each will be subjected to an overcharge at long and short orbit current densities.

Four cells are being subjected to extended periods of trickle charging (i.e. 150 days) to investigate the pressure decay which occurs after the initial pressure buildup. The cells which exhibit the best rates of recombination will be put on orbital cycling regimes. No results are available as yet.

### Phase 3

The loss of argentic voltage on discharge as a result of constant potential charging is being investigated in this phase. It seems that the effect may be due to an increase in resistance caused by increasing conversion of free silver to argentic oxide. Argentous oxide is probably not involved, although its resistivity is high, because, it is known that silver goes essentially directly to the argentic oxide if the charging voltage is high enough. Another possibility is the change in lattice dimensions and material properties as the oxygen content increases beyond that corresponding to  $\text{Ag}_2\text{O}$ .

A series of cells containing one positive and two negatives have been built and put on a c.p. charge to be continued for ten weeks. At present they have completed six weeks on "float". The expanded metal grids in the positives vary in conductivity from cell to cell; the intent is to disclose whether the disappearance of the argentic voltage is associated with conductivity. One cell contains a lead additive in the positive; lead was incorporated because of its ability to form a semi-conductor on oxidation.

After ten weeks the cells will be discharged at the 6 hour rate to determine whether there is any argentic oxide retention in the positive electrode.

A second group of cells will be started on this c.p. charging. This group will be dissected for analyses as follows:

1. Determination of  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  by the polarographic method successfully used on plates which have not been overcharged. It is not known, at this point, how silver charged beyond the  $\text{Ag}_2\text{O}$  level will react.
2. Determination of oxygen content by weight loss.
3. Examination of the lattice by X-ray.
4. Measurement of plate conductivity and comparison with standard charged plates.
5. Potentiostatic discharge. Characteristics will be compared with those of plates charged at other potentials.

#### Phase 4

The main objectives in operating on the argentous plateau are, to avoid gassing at the end of charge, to decrease the difference between charge and discharge voltages and to discharge at a more nearly constant voltage. The silver which is ordinarily used in silver-cadmium cells will accept only about 30% of its total charge on the argentous level. To operate a cell with this type of silver and still maintain good argentous efficiency would require that the silver content be increased by a factor 10/3. Such a modification would be undesirable because of the increased cost and loss of energy density (WH/g).

To counter this difficulty, three avenues are being explored. The first is the use of fine grain silver which gives a much longer argentous plateau than our standard powders; the second is the use of palladium as an additive, and the third is the use of a specially treated, highly porous sintered supporting matrix for the silver.

The principal problem is the retention of the desired discharge and charge characteristics. This is known from previous work in other and in our laboratories which has shown that these characteristics decrease and eventually disappear with continued cycling. This disappearance has been attributed to recrystallization of the silver. Where palladium is used, it is also possible that the palladium has changed in form. We plan to study these possibilities using the double layer capacitance method to determine surface area changes, and analytical techniques for palladium changes.

The first group of cells which was built included fine grain silver powders, (0.5 to 2.0 microns), grids of various conductivities, two separator systems, and several electrolyte concentrations. These last were included because of the effect on solubility of argentous oxide. Table V summarizes the combinations. The cells were given one formation deep cycle; twelve additional cycles were run to determine the maximum  $\text{Ag}_2\text{O}$  efficiency attainable with the various cell constructions. All charges were carried out until the first break was observed; the cells were discharged to an end voltage of 0.6. Table VI shows the capacity data for each cell. The weight of active silver contained in each cell, corresponded to the theoretical argentous oxide capacity of 2.75 AH. It can be seen from the data that the maximum  $\text{Ag}_2\text{O}$  capacity was attained on the first cycle, and by cycle 12 all save for one cell were below 20% of the theoretical argentous capacity. Cognizance must be taken of the fact that initially the cells only delivered between 3.6 and 4.5 ampere hours on both levels. In view of this, the performance of cell 91 which is performing at 62% of its original argentous capacity (see Figure 5) can be considered fairly satisfactory. The principal difference in the composition of this cell is the 25% KOH electrolyte. We have scheduled additional cells with concentrations bracketing 25% to verify the effect and determine whether it may be greater at some other concentration.

For the present, however, cell 91 will be given a few conditioning (deep) cycles, and then placed on the 100 minute orbit regime. The effect of palladium, nickel, and lead as positive additives for increasing the  $\text{Ag}_2\text{O}$  capacity will also be investigated shortly following completion of cell construction. There will be particular emphasis on the use of 25% KOH.

The use of a highly porous sintered matrix as the supporting grid for silver had been reported prior to this work by both Gulton Industries and Delco-Remy. However, although the ratio of argentic to argentous voltage on discharge was impressive, other facets of the performance were less satisfactory. Severe gassing on charge was reported and capacity data indicated relatively low utilization of the silver.

In the attempt to overcome these difficulties, nickel plaques were impregnated with a saturated solution of  $\text{AgNO}_3$  at  $80^\circ\text{C}$ , after which one was plated with 0.1% lead. The electrodes were then placed in alkali to convert the nitrate salt to argentous oxide; following this treatment they were placed in dummy cells and given five cycles. Figures 6 and 7 illustrates the performance data.



It can be seen that both electrodes give better than 90% of theoretical utilization. The lead-treated electrode however, yields 42% of its energy on the argentic level during discharge and about the same percentage on the argentous plateau during charge. These results show the possibility of using this type of plate on either upper or lower voltage levels. Its use on the  $\text{Ag}_2\text{O}$  portion seems preferable at present because the possibility of oxygen evolution is eliminated at this voltage. It should be pointed out here that the gas evolution voltage was no lower on the lead-treated plate than on a standard silver plate. A second method of impregnation was also tried, using a solution containing silver nitrate plus lead nitrate followed by co-precipitation of both oxides in 31% KOH. After three dummy cycles the results are comparable with those obtained by the lead plating method. Cells which feature the above types of positive plates are presently being constructed and will begin cycling during this quarter. These cells will more fully determine the parameters for both construction and cycling regimes.

#### PROGRAM FOR NEXT QUARTER

##### Phase 1

Complete deep cycles at various temperatures, and start cells on orbital cycling regimes. Study changes in surface area of plates by means of double layer capacitance, and by BET gas adsorption.

##### Phase 2

Start gas recombination work in special chamber and in cells. Compare recombination rates in cells with Cd impregnated nickel plaques standard CdO plates with Aldex paper and cell without Aldex paper around negative.

Study the mechanism of oxygen recombination using polarographic and potentiostatic methods. Study oxygen recombination rates in cells and the special chamber.

##### Phase 3

Continue constant potential charging on single electrode cells. Initiate potentiostatic investigation of reactions occurring at the positive electrode during cp anodization.

##### Phase 4

Complete construction of cells with palladium and silver impregnated Ni plaques; start cells on short orbit regime. Determine optimum weight of silver in nickel plaque. Study gassing rate of these cells on both the  $\text{AgO}$  and  $\text{Ag}_2\text{O}$  levels.

TABLE I

## POSITIVE DUMMY ELECTRODE PERFORMANCE

| CELL | RT   |      |      | +50°C |                |      | RT   |                     |      | -15°C               |                     |                   | RT                |      |      | REMARKS |                       |
|------|------|------|------|-------|----------------|------|------|---------------------|------|---------------------|---------------------|-------------------|-------------------|------|------|---------|-----------------------|
|      | ①    | ②    | ③    | ④     | ⑤              | ⑥    | ⑦    | ⑧                   | ⑨    | ⑩                   | ⑪                   | ⑫                 | ⑬                 | ⑭    |      |         |                       |
| 1    | 1.95 | 1.9  | 1.37 | 1.2   | 1.45           | 1.25 | 1.40 | 1.30                | 1.47 | CELL SHORTED - CY 6 | 1.25                | 1.0               | .85               | 1.48 | 1.70 | 1.26    | "HC" - 4.8g/cc 31% KO |
| 2    | 1.36 | 1.27 | 1.22 | 1.37  | 1.31           | 1.7  | 1.5  | 1.71                | 1.60 | 1.53                | 1.52                | 1.53              | 1.3               | 1.32 | 1.76 | 1.45    | " " " " "             |
| 3    | 1.8  | 2.0  | 1.4  | 1.35  | .3             | 1.02 | .3   | CELL SHORTED - CY 4 | 1.35 | 1.44                | 1.32                | .85               | .82               | .76  | .70  | 1.45    | " " " " 36.5% "       |
| 4    | 1.35 | 1.20 | 1.18 | 1.48  | 1.41           | 1.46 | 1.4  | 1.65                | 1.60 | 1.5                 | 1.35                | 1.44              | 1.32              | .85  | .82  | 1.45    | " " " " "             |
| 5    | 1.7  | 1.95 | 1.1  | 1.39  | 1.2            | 1.45 | 1.25 | 1.4                 | 1.65 | 1.50                | CELL SHORTED - CY 6 | 1.23              | 1.29              | .2   | .8   | .83     | " " " " 42% "         |
| 6    | 1.32 | 1.20 | 1.0  | 1.35  | 1.35           | 1.36 | 1.33 | 1.63                | 1.57 | 1.35                | 1.23                | 1.29              | .2                | .8   | .83  | 1.45    | " " " " "             |
| 7    | 1.85 | 1.95 | 1.57 | 1.45  | SHORTED - CY 3 |      |      |                     |      |                     |                     |                   |                   |      |      |         | " " " " 4.2g/cc "     |
| 8    | 1.02 | .93  | .89  | 1.20  | 1.1            | 1.42 | 1.30 | 1.46                | 1.56 | 1.36                | 1.21                | 1.28              | .3                | .8   | .7   | 1.42    | " " " " "             |
| 9    | 1.77 | 1.91 | 1.25 | 1.45  | SHORTED - CY 3 |      |      |                     |      |                     |                     |                   |                   |      |      |         | " " " " 3.6g/cc "     |
| 10   | 1.27 | .95  | .95  | 1.3   | 1.17           | 1.28 | 1.13 | 1.52                | 1.6  | 1.41                | 1.3                 | 1.42              | 0                 | 0    | 0    | 1.35    | " " " " "             |
| 11   | 1.2  | 1.35 | 1.4  | 1.45  | .95            | 1.5  | 1.2  | 1.4                 | 1.26 | 1.45                | 1.41                | .5                | CELL SHORTED CY 7 |      |      |         | "HANS" - 4.8g/cc "    |
| 12   | 1.38 | 1.37 | 1.3  | 1.41  | 1.34           | 1.43 | 1.33 | 1.27                | 1.23 | 1.2                 | 1.13                | 1.2               | .2                | .85  | .87  | 1.61    | " " " " "             |
| 13   | 1.92 | 1.95 | 1.15 | 1.27  | 1.14           | 1.45 | 1.1  | 1.22                | 1.09 | 1.45                | .9                  | CELL SHORTED CY 6 |                   |      |      |         | " " " " " "           |
| 14   | 1.11 | .8   | .9   | .94   | .91            | 1.28 | 1.1  | 1.3                 | 1.3  | 1.44                | 1.27                | .85               | 0                 | 0    | 0    | 1.1     | " " " " " "           |

ID + IS

EVEN NO - .51A .34A - SHORT CIRCUIT

ODD NO. .70A .03A - LONG CIRCUIT

PLATE SIZE = 2 1/16" x 1 1/4"

4.2g Ag/plate

TABLE II

CHANGE OF SURFACE AREA WITH CYCLING  
(SHORT ORBIT, LONG ORBIT)

| TYPE OF Ag PWD.  | DENSITY-g/cc | SURFACE AREA- $m^2/g$ |                                |                               |
|------------------|--------------|-----------------------|--------------------------------|-------------------------------|
|                  |              | PRIOR TO CYCLING      | AFTER CYCLING<br>(SHORT ORBIT) | AFTER CYCLING<br>(LONG ORBIT) |
| HAMS             | 4.8          | 0.235 (298)           | 4.70 (5900)                    | 7.6 (9500)                    |
| HC               | 4.8          | 0.320 (395)           | 18.0 (23000)                   | 4.75 (6000)                   |
| "                | 4.2          | 0.365 (462)           | 13.0 (15,600)                  | PLATE CRUMBLER                |
| "                | 3.6          | 0.378 (500)           | 5.7 (6700)                     | 4.3 (5400)                    |
| FE**             | 4.8          | 0.900 (1100)          | 7.6 (9300)                     | 6.1 (7600)                    |
| "G-7"-HOT FORGED | 4.2          | NO DATA AVAILABLE     | 21.3 (SPECIAL REGIME)          |                               |

THE VALUES IN ( ) DENOTE THE RECOMBINATION FACTOR FOR EACH ELECTRODE.

TABLE III  
ELECTROLYTE ANALYSES

| CELL NO. | 25°C + 50% DEPTH DISCHARGE |   | FREE KOH(%) |
|----------|----------------------------|---|-------------|
|          | TOTAL ALKALINITY(%)        | *K <sub>2</sub> CO <sub>3</sub> (mg/ml) |             |
| 117      | 37.3                       | 202                                     | 27.6        |
| 122      | 37.5                       | 214                                     | 27.1        |
| 123      | 37.8                       | 134                                     | 36.2        |
| 124      | 38.7                       | 182                                     | 36.0        |
|          | 50°C + 25% DEPTH DISCHARGE |   |             |
| 285      | 35.5                       | 302                                     | 19.4        |
| 286      | 35.1                       | 422                                     | 11.6        |
| 287      | 36.2                       | 428                                     | 17.4        |
| 288      | 36.5                       | 333                                     | 18.7        |
| 289      | 35.7                       | 380                                     | 14.9        |
| 290      | 35.2                       | 403                                     | 12.9        |
| 291      | 35.0                       | 428                                     | 10.7        |
| 292      | 35.0                       | 428                                     | 10.7        |

\* K<sub>2</sub>CO<sub>3</sub> DENDOTES ALL THE SALTS TITRATED BETWEEN THE  
PHENOLPHTHALEIN AND METHYL ORANGE END POINTS.

TABLE IV  
SILVER ANALYSES

| ** CELL NO.  | 25°C + 50% DEPTH DISCHARGE |        |               |  | 2ND LAYER C19 |
|--------------|----------------------------|--------|---------------|--|---------------|
|              | 2 LAYERS OF NYLON          | PVA    | 1ST LAYER C19 |  |               |
| 117          | 24.3                       | 83.5   | 0.4           |  | 0.2           |
| 122          | 12.6                       | 76.7   | 0.3           |  | 0.2           |
| 123          | 3.6                        | 52.8   | 0.2           |  | 0.1           |
| 124          | 10.9                       | 72.5   | 0.7           |  | 0.3           |
| 50°C + 25% D |                            |        |               |  |               |
| 285          | 83.5                       | (29.6) | 21.3          |  | 1.0           |
| 286          | 67 *                       | (12)   | 41.4 *        |  | .5            |
| 287          | 75.6 *                     | (16.3) | 30.6 *        |  | 2.1           |
| 288          | 74.5                       | (49.1) | 6.3           |  | .2            |
| 289          | 74.3 *                     | (16.3) | 36 *          |  | 3.6           |
| 290          | 75.5                       | (25.2) | 2.8           |  | 1.7           |
| 291          | 103 *                      | (32.3) | 2.5 *         |  | .2            |
| 292          | 62                         | (22.3) | 26.9          |  | 1.3           |

ALL VALUES ARE EXPRESSED IN MILLIMETER PER SQUARE INCH.

\* SINCE SOME PVA MAY HAVE CHARGED TO THE NYLON OR C19 OR BOTH, THE SILVER CONTENT OF THESE MAY BE ON THE HIGH SIDE.

\*\* CELLS SUPPLIED BY INLAND TESTING CORP.

TABLE V  
PHASE 4 - GROUP 1

| CELL NO. | SILVER POWDER   | SER. SYSTEM         | GRID   | ELECTROLYTE CONC. |
|----------|-----------------|---------------------|--------|-------------------|
| 82       | HC - UNSINTERED | 2NY/60VH/(-)        | Ag-4/0 | 42% KOH           |
| 83       | "               | "                   | "      | "                 |
| 84       | "               | POWDER SINTERED     | Ag-1   | "                 |
| 85       | "               | - NO PLATE SINTERED | Ag-4/0 | "                 |
| 86       | "               | "                   | "      | "                 |
| 87       | FR (NO SINTER)  | 2NY/30VH/(-)        | Ag-1   | 36.5% KOH         |
| 88       | "               | "                   | "      | 42%               |
| 89       | "               | "                   | Ag-4/0 | 36.5% KOH         |
| 90       | "               | "                   | "      | 42%               |
| 91       | "               | 2NY/30VH/(-)        | Ag-1   | 25%               |
| 92       | "               | "                   | "      | 31%               |
| 93       | "               | "                   | "      | 36.5%             |
| 94       | "               | "                   | "      | 42%               |
| 95       | "               | "                   | Ag-4/0 | 36.5%             |
| 96       | "               | "                   | "      | 42%               |
| 97       | MR (.5mm)       | "                   | "      | "                 |

ALL PLATES FLEESSED TO 4.5 μ KC DENSITY

**TABLE VI**  
\*CYCLE DATA - PHASE 4 GROUP 1

| CYCLE No. | 82   | 83   | 84   | 85  | 86   | 87   | 88   | 89   | 90   | 91   | 92   | 93   | 94   | 95   | 96   | 97   |
|-----------|------|------|------|-----|------|------|------|------|------|------|------|------|------|------|------|------|
| F-1       | 3.83 | 3.6  | 3.8  | 4.0 | 3.95 | 4.0  | 4.0  | 4.15 | 4.3  | 3.75 | 3.9  | 4.0  | 4.35 | 4.3  | 4.5  | 3.7  |
| * 2       | 1.05 | 1.1  | 1.15 | 1.1 | 1.1  | 1.4  | 1.75 | 1.5  | 1.55 | 1.6  | 1.6  | 1.55 | 1.70 | 1.45 | 1.60 | 1.35 |
| 3         | 1.1  | 1.15 | 1.15 | 1.0 | 1.2  | 1.45 | 1.3  | 1.0  | .75  | 1.2  | 1.1  | 1.1  | .80  | .85  | .85  | .70  |
| 4         | .80  | .80  | .95  | .70 | .85  | 1.30 | .25  | .35  | .70  | 1.25 | 1.20 | .95  | 1.0  | .80  | .80  | .65  |
| 5         | .70  | .65  | .75  | .60 | .80  | .90  | .75  | .80  | .55  | 1.10 | .95  | .80  | .75  | .60  | .60  | .40  |
| 6         | .65  | .75  | .75  | .60 | .80  | .90  | .80  | .70  | .50  | 1.15 | .95  | .65  | .70  | .60  | .60  | .50  |
| 7         | .60  | .60  | .70  | .60 | .70  | .80  | .60  | .70  | .50  | 1.10 | .90  | .60  | .65  | .60  | .60  | .40  |
| 8         | .55  | .55  | .70  | .50 | .70  | .70  | .50  | .60  | .50  | 1.10 | .80  | .55  | .55  | .50  | .50  | .30  |
| 9         | .50  | .55  | .60  | .50 | .55  | .65  | .45  | .55  | .40  | 1.05 | .70  | .50  | .50  | .45  | .45  | .35  |
| 10        | .53  | .55  | .58  | .50 | .55  | .70  | .50  | .60  | .40  | 1.21 | .80  | .53  | .50  | .50  | .50  | .30  |
| 11        | .50  | .57  | .60  | .50 | .60  | .65  | .60  | .55  | .40  | 1.15 | .80  | .50  | .50  | .50  | .50  | .40  |
| 12        | .50  | .60  | .60  | .50 | .60  | .70  | .50  | .50  | .45  | 1.15 | .75  | .50  | .50  | .50  | .50  | .35  |

\* ONLY HHQ DATA ARE PRESENTED

\*\* CY 2-12 CHANGED TO 1.35 VOLTS

# LOSS OF ACTIVE MATERIAL POSITIVE DUMMY ELECTRODES (AFTER DEEP CYCLES)

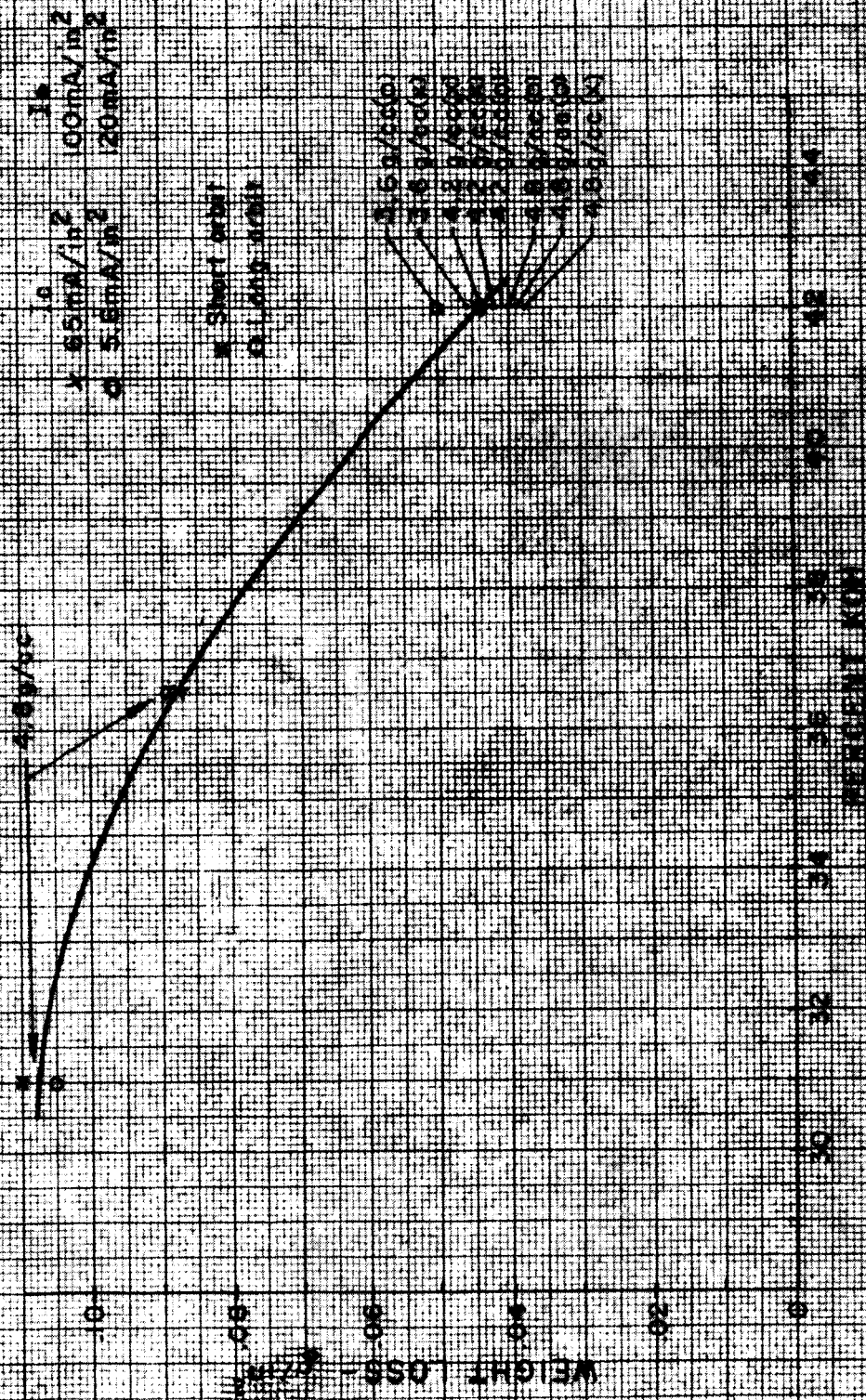


FIG. 1.



# ELECTRO-PLATED CADMIUM NEGATIVE

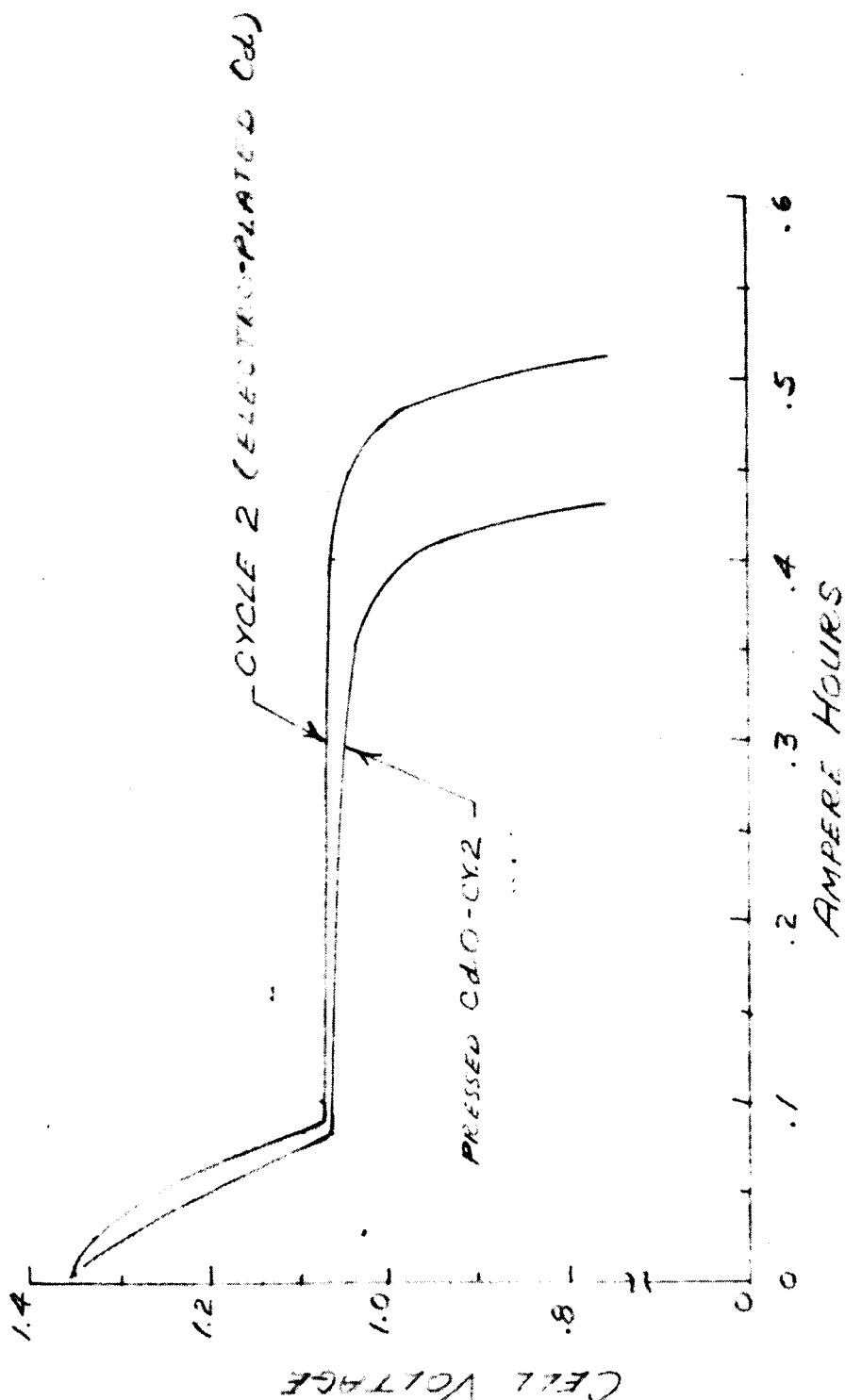
1 NEG/2 POS CELL

AREA = 3.75 IN<sup>2</sup>

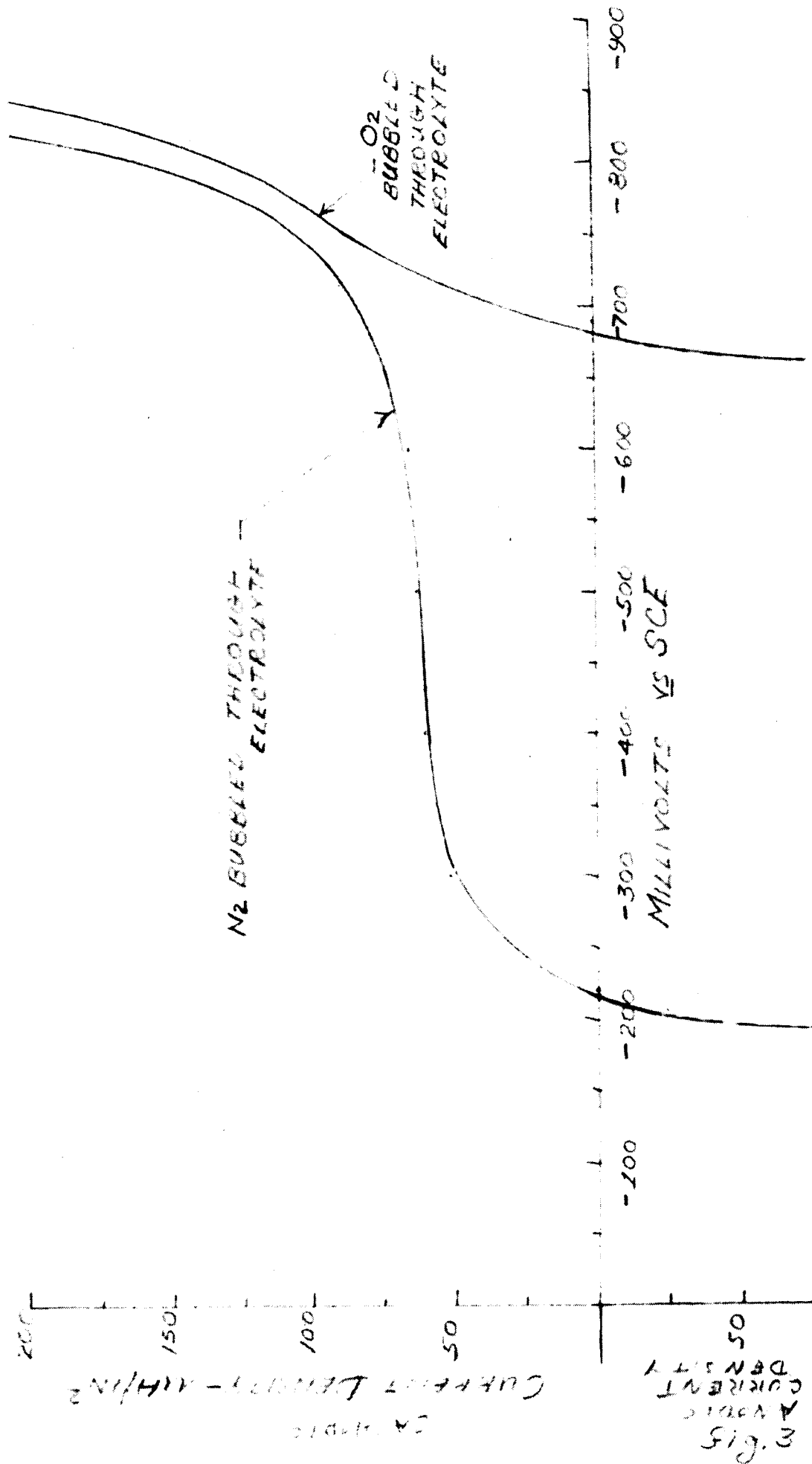
WT Cd = 1.9g

DENSITY = 3.0g/cc

CURRENT = 1.85 A



# REDUCTION OF O<sub>2</sub> ON Cd SHEET ELECTRODE



# REDUCTION OF OXYGEN ON MERCURY ELECTRODE

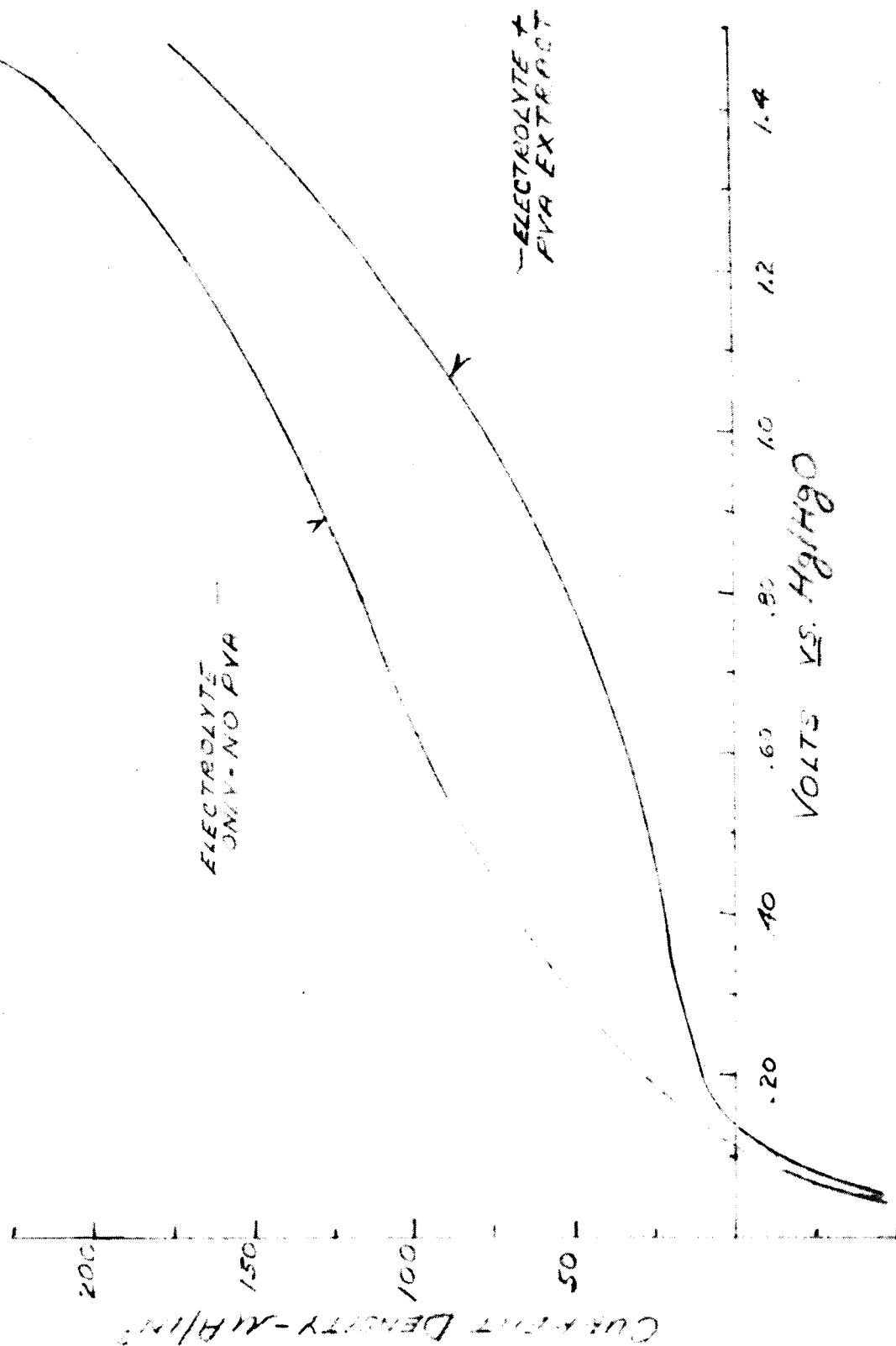


Fig. 4

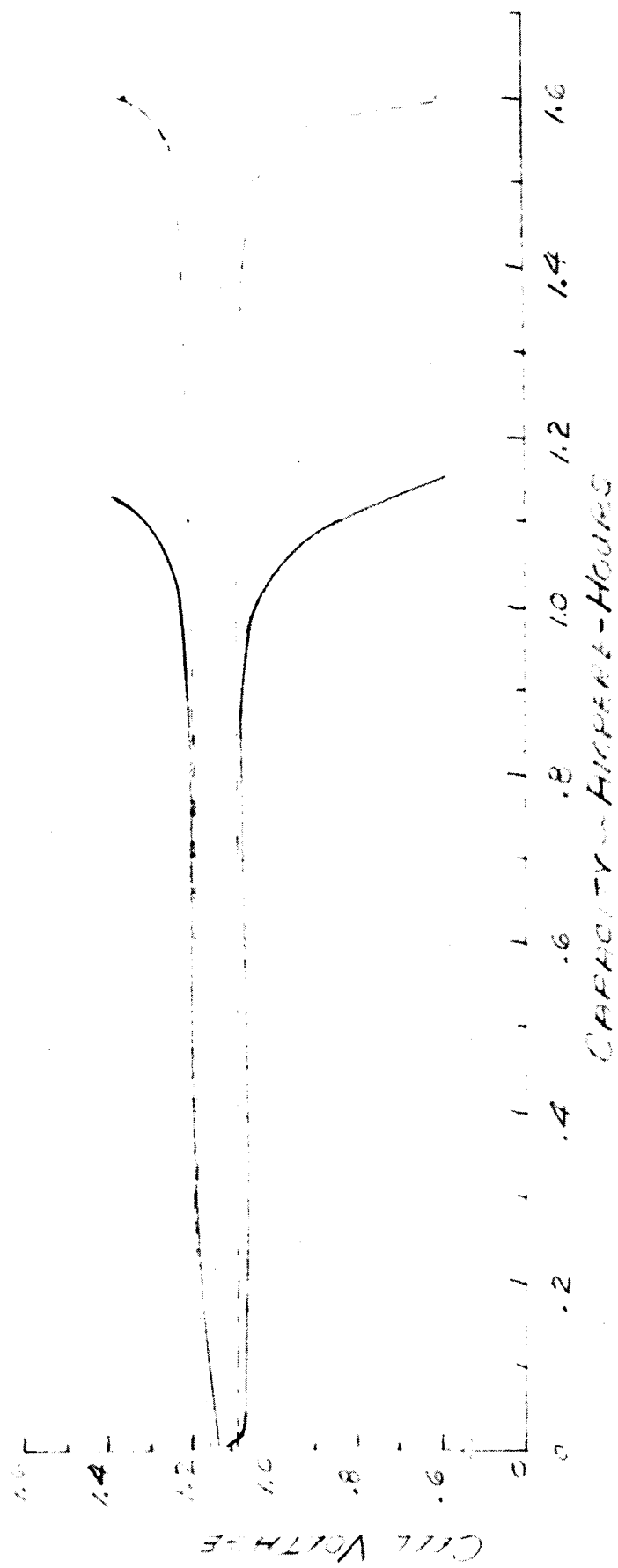
# DISCHARGE-CHARGE PERFORMANCE

(CELL 91)

DISCHG - .42A → 0.6V

CHG - .26A → 1.35V

--- CYCLE 2  
— CYCLE 12



# AgNO<sub>3</sub> IMPREGNATED NICKEL PLAQUE

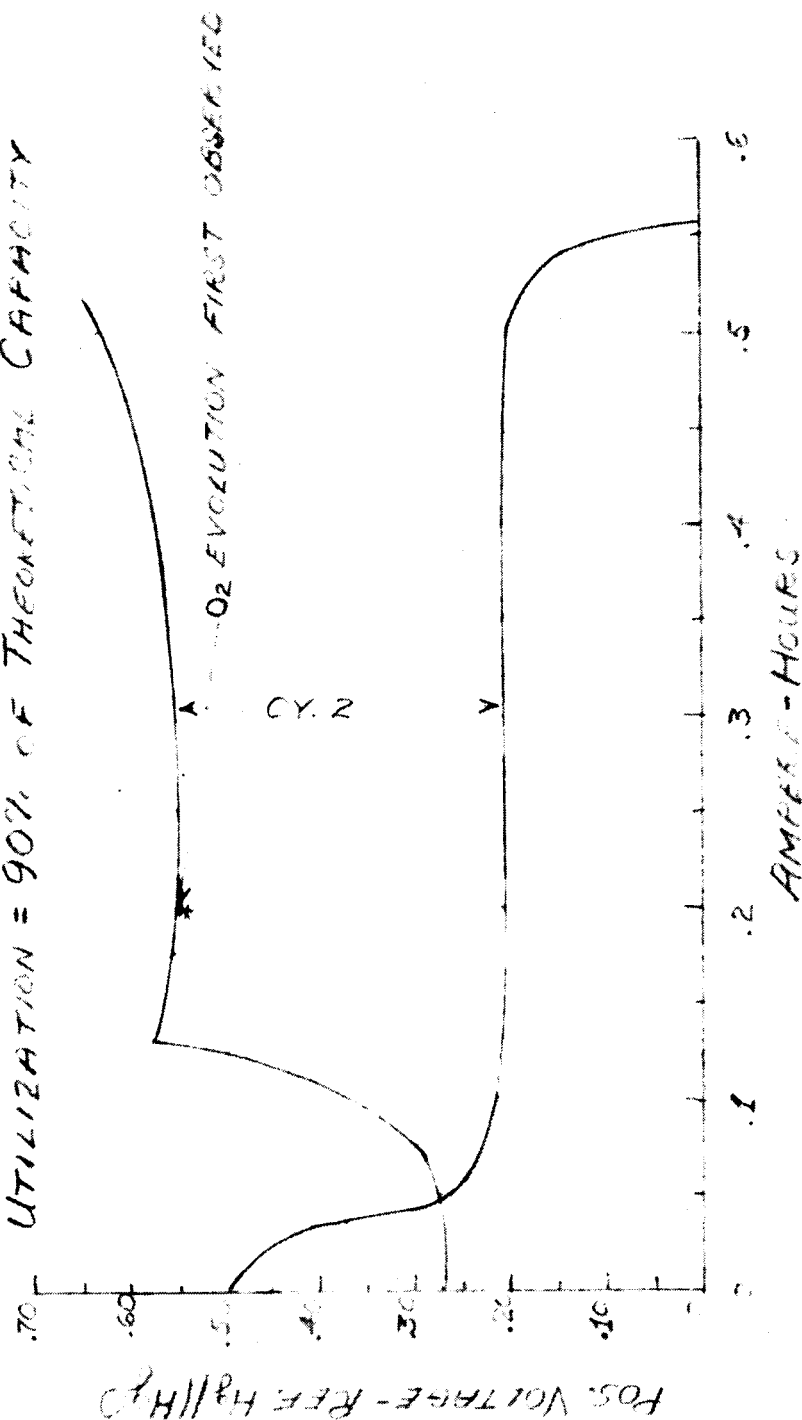
20 VOLT = 60 MA/IN<sup>2</sup> (300 MA)

PLATE AREA = 5 IN<sup>2</sup>

WT. AG = 1.29 g

ELECTROLYTE = 31% KOH

UTILIZATION = 90% OF THEORETICAL CAPACITY



$\text{AgNO}_3$  INFREGNATED NICKEL PLATUE + 0.1% Pb  
 DENSITY 300 MA (60 MA/IN<sup>2</sup>)  
 PLATE = 2" x 1 1/4" = 5.0 IN<sup>2</sup>  
 WT Ag = 1.30 g / PLATE  
 ELECTROLYTE = 31% KOH  
 UTILIZATION = 92% OF THEORETICAL CAPACITY

